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Introduction

➢ There is growing interest in cobalt metal and cobalt silicide films in logic and memory devices, especially for Co capping layer application. It is now well established that the Co capping layer formed on the Cu interconnect (as opposed to the low-*k* dielectric) significantly improves the top interface of the Cu lines for electromigration (EM) resistance[1]. In addition, $CoSi_2$ offers the advantage of substantially lower resistance and physical and electrical compatibilities with Si so that it could be potentially used in CMOS for source and drain contact metals and other Si nanowire devices[2]. The Co precursor selection for CVD and ALD is primarily based on good thermal stability, high reactivity, the ease of deposition of Co, and precursor delivery technique including Direct Liquid Injection process (DLI).

➢ For CVD and ALD of cobalt, various sources such as $Co_2(CO)_8$, (*tert*-butyl acetylene) $Co_2(CO)_6$, (allyl)$Co(CO)_3$, and $Co(THD)_2$ were used before with limited success[1-3]. Most recently, a cobalt amidinate precursor[4] has been investigated. In this study, we report the successful use of cobalt amidinate precursor (*i.e.*, Co-AMD) along with several novel cobalt formamidinate precursors (*i.e.*, Co-FAMD). The results evidently show that Co-AMD as well as Co-FAMD offer significant advantages over conventional precursors in terms of their higher vapor pressures and greater thermal stabilities.

➢ The physical properties of these sources, such as solubility, volatility, thermal stability, chemical compatibility, and viscosity will be discussed. Results showing the high purity of the sources based on ICP-MS and FT-NMR analyses will be reported, along with the characterization of the thermal stabilities with supporting TGA, ARC, and FT-NMR analysis. Preliminary ALD and CVD results of Co metal deposition using the new sources will be discussed, using Vapor-Draw process.

References

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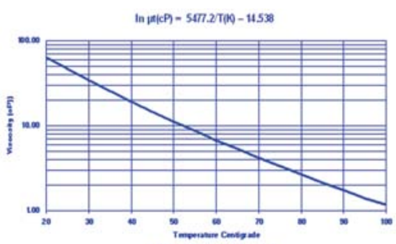
Cobalt Alkyl Amidinates (Co-1 and Co-2)

Co-1:
- A deep greenish liquid precursor at room temperature with high vapor pressure
- Vapor cobalt source < 80°C
- Thermally stable liquid cobalt source at delivery temperature
- Highly reactive towards ammonia, air and moisture

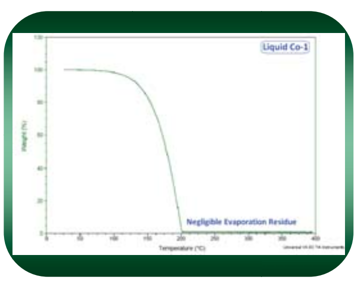
Co-2:
- A dark greenish solid precursor at room temperature with high vapor pressure
- Melted at 84°C giving a liquid cobalt source at delivery temperature of > 90°C
- Highly thermally stable up to 250°C

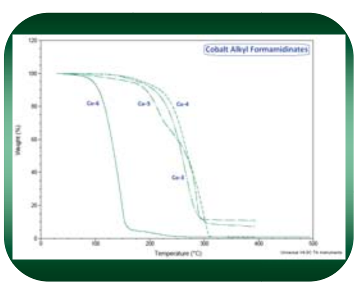
Viscosity of Liquid Co-1



< 10 cP at > 50 degree C
Applicable for selected DLI system

TGA of Liquid Co-1 and Cobalt Alkyl Formamidinates (Co-3, Co-4, Co-5, Co-6)





Cobalt Alkyl Formamidinates (Co-3, Co-4, Co-5 and Co-6)

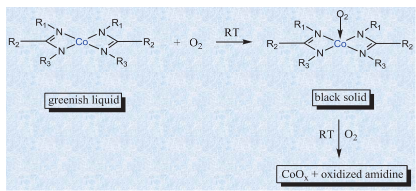
Cobalt Formamidinates (Co-3, Co-4, Co-5, Co-6):

- All cobalt alkyl formamidinates were greenish or purple crystalline materials owing to their dimeric structures.
- Co-3 and Co-4 were surprisingly air stable while Co-5 and Co-6 were air sensitive but at a much lesser degree than Co-1 and Co-2.
- Soluble in organic solvents, very good cobalt source for DLI
- Highly thermally stable with high volatility

Thermal Stress Test on Liquid Co-1 and Co-2

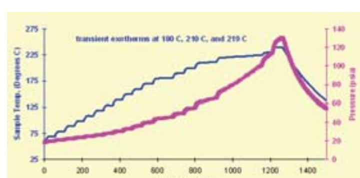
Thermal Stress Test of Liquid Co-AMD at 120°C for 60 hours

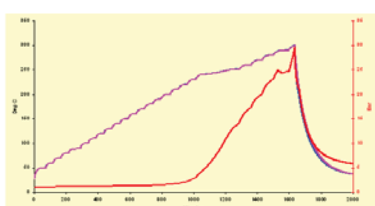
Sample	Thermal Condition	316 SS metal pieces	^{1}H NMR Analysis
liquid Co-AMD	120°C	none	no organic impurities detected
liquid Co-AMD	120°C	freshly treated w/ acid	no organic impurities detected
liquid Co-AMD	120°C	aged at 150°C	no organic impurities detected



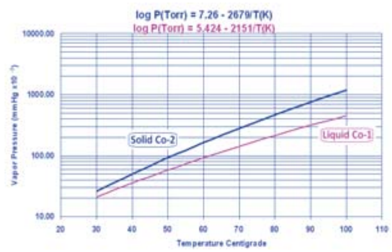
Accelerated Rate Calorimetry (ARC) Study on Liquid Co-1 and Co-2

Temperature/Pressure vs. Time Curves:
- For liquid Co-1, slow, non-sustaining, transient exotherms observed at 180, 210, and 219°C, a good indication showing higher surface reactivity of liquid Co-1; Some non-condensable gas generated starting at 219°C
- For solid Co-2, an exotherm onset at 240°C with pressure buildup spontaneously



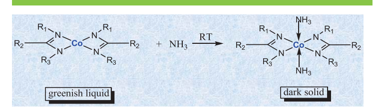


Vapor Pressure of Co-1 and Co-2



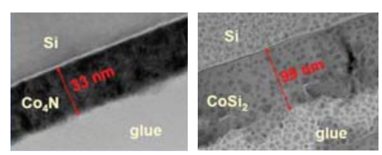
Reactivity of Liquid Co-1 with NH_3, Air, and $Co_2(CO)_8$

Liquid Co-1:
- Ammonia coordinated with Co-1 spontaneously and turned liquid Co-1 into a dark solid material at room temperature.
- Oxygen reacted with Co-1 spontaneously and turned liquid Co-1 into a black solid material immediately followed by fully oxidizing process forming a dark brownish solid material.
- Liquid Co-1 was not chemically compatible with $Co_2(CO)_8$, and dissociated CO from $Co_2(CO)_8$ coordinated to Co-1 yielding a dark solid material.



Thin Film Processing Performance

Liquid Co-1:
- Low temperature thermal CVD or ALD with H_2 or H_2/NH_3 giving highly pure Co films
- Thermal CVD growth rates over 3 nm/min while thermal ALD growth rates up to 0.5 Å/cycle
- Low temperature thermal CVD/ALD with NH_3 giving Co_4N (resistivity at 102 µΩ·cm) at 180°C, further annealed to form $CoSi_2$ at 630°C (resistivity at 21 µΩ·cm near bulk value of 15-20 µΩ·cm)



Conclusions

- New cobalt sources (liquid Co-1, Co-2, Co-3, Co-4, Co-5, and Co-6) were successfully developed as the choices of Co precursors for deposition of Co and $CoSi_2$ thin-films by ALD and CVD.
- Those Cobalt precursors were also designed to be Co sources for direct liquid injection delivery for ALD and CVD.
- The new cobalt precursors were successfully demonstrated to grow metallic Co and $CoSi_2$ films at lower temperature, particularly for liquid Co-1.

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